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# Ternary chlorides in the systems $ACl/HoCl_3$ (A=Cs, Rb, K)<sup>1</sup>

M. Roffe, H.J. Seifert\*

Inorganic Chemistry, University GH Kassel, H. Plett-Str. 40, D-34109 Kassel, Germany

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## Abstract

The phase diagrams of the pseudo-binary systems  $ACl/HoCl_3$  (A=Cs, Rb, K) were investigated by DTA and XRT. The existence of compounds  $A_3HoCl_6$ ,  $Cs_2HoCl_5$ ,  $Cs_3Ho_2Cl_7$  and  $AHo_2Cl_7$  could be confirmed. Additionally, the 2:1-compounds  $Rb_2HoCl_5$  ( $Cs_2DyCl_5$ -structure) and  $K_2HoCl_5$  ( $K_2PrCl_5$ -structure) were found. By solution enthalpy and e.m.f vs. *T* measurements in galvanic chlorine cells for solid electrolytes, the thermodynamic functions for the formation from ACl and HoCl<sub>3</sub> and for the formation from the compounds adjacent in the phase diagrams were measured.

The compounds  $A_3HoCl_6$  could be prepared also from acetic acid solutions. From aqueous solutions, the ternary halides  $Cs_4HoCl_7$  and  $Cs_3HoCl_6$  crystallizing in the space group *Pbcm* were prepared. Anhydrous HoCl\_3 can be obtained comfortably from holmium formiate at ~300 °C in an HCl gas stream. © 1997 Elsevier Science S.A.

Keywords: Ternary holmium chlorides; Phase diagrams; Thermodynamic properties; Preparations from acetic and formic acid

#### 1. Introduction

In the course of investigations on the existence of ternary lanthanide chlorides  $A_n LnCl_{n+3}$  (A=Cs, Rb, K) we had found that the decline of coordination number (CN) for the lanthanide ions with decreasing ionic radius depends also on the size of the A<sup>+</sup> ions. For the group  $A_2LnCl_5$ , e.g., the change from CN 7 ( $K_2PrCl_5$ -type [1]) to CN 6 ( $Cs_2GdCl_5$  [2]) occurs between Ln=Nd [3] and Sm [4] in the case of A=Cs, while Rb compounds with the  $K_2PrCl_5$ -structure exist up to Rb<sub>2</sub>GdCl<sub>5</sub> [5]; an analogous Tb compound is no longer stable [6].

Thus, it was of interest to find out whether this tendency continues on going to still smaller lanthanide ions. In this paper our observations on the systems  $ACl/HoCl_3$  (A=Cs, Rb, K) are reported. From the literature, the only investigation on the system KCl/HoCl\_3 [7] describes only two compounds: K<sub>3</sub>HoCl<sub>6</sub> and KHo<sub>2</sub>Cl<sub>7</sub>. Unit cell dimensions for such compounds, which can be prepared without quenching/annealing, were given by Meyer [8].

#### 2. Experimental

## 2.1. Chemicals

Starting compound was  $HoCl_3 \cdot 6H_2O$ , prepared from a solution of  $Ho_2O_3$  (99.9%, Heraeus, Hanau) in hot hydrochloric acid. Alkali metal chlorides were dried at 500 °C.

# 2.2. Differential thermal analysis (DTA)

The DTA measurements were performed in a home-built device for samples (~0.5 g) in vacuum-sealed silica ampoules. In general, heating curves were recorded (heating rate=2 °C min<sup>-1</sup>). Because HoCl<sub>3</sub> melt reacts with silica, only samples up to 80 mol% HoCl<sub>3</sub> were measured. HoCl<sub>3</sub> rich mixtures were melted in the DTA furnace approx. 20 ° above the alleged liquidus temperatures, homogenized by shaking and annealed. Mixtures with less than 50 mol% HoCl<sub>3</sub> were melted in a gas flame.

## 2.3. X-ray powder patterns

Powder patterns at ambient temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (Cu-K $\alpha$  radiation) the samples were kept under He atmos-

<sup>\*</sup>Corresponding author.

<sup>&</sup>lt;sup>1</sup>Dedicated to Professor Roger Blachnik on the occasion of his 60th birthday.

phere. For high-temperature photographs a Simon-Guinier camera (Enraf-Nonius) was applied. Corundum powder was used as the internal standard; at 20 °C; a=475.92 pm, c=1299.00 pm; at 500 °C, a=479.32, c=1308.92 pm.

#### 2.4. Solution calorimetry

The home-built isoperibolic calorimeter for samples of 2–4 g, dissolved in 1.1 l is described elsewhere [9]. From the enthalpies of solution,  $\Delta_{sol}H_{298}^{\circ}$ , the formation enthalpies of the ternary chlorides from  $nAC1+HoCl_3$ ,  $\Delta_{f}H_{298}^{\circ}$ , were calculated, according to:

$$\Delta_{\rm f} H^{\circ} = \{\Delta_{\rm sol} H^{\circ}({\rm HoCl}_{3}) + n \Delta_{\rm f} H^{\circ}({\rm ACl})\}$$
$$- \Delta_{\rm sol} H^{\circ}(A_{n} {\rm HoCl}_{3+n})$$

## 2.5. E.m.f. measurements

A detailed description of the galvanic cell was given previously [10]. The measured potentials were generated by solid state reactions:

$$n \operatorname{ACl} + A_{x} \operatorname{HoCl}_{3+x} = A_{(n+x)} \operatorname{HoCl}_{(3+x+n)}$$

in the temperature range of 300-400 °C. The solid electrolytes (compressed disc) were separated by an A<sup>+</sup> conducting diaphragm of sintered glass powder. The collected e.m.f vs. *T* values could be subjected to a linear regression analysis: e.m.f./mV=a+bT/K.

#### 3. Results

## 3.1. Holmium (III) chloride

 $HoCl_3 \cdot 6H_2O$  loses water at ~70 °C, forming a dihydrate. Further dehydration to  $HoCl_3 \cdot H_2O$  at 100–120 °C and to anhydrous  $HoCl_3$  at 180–200 °C must be performed in an HCl gas stream to avoid hydrolysis. For a sample of 10 g, the last step needs three days of slow temperature elevation.

The peril of hydrolysis can be diminished when heating Ho formiate in HCl gas at 300 °C. Ho(HCOO)<sub>3</sub> is formed as a pink precipitate from a hot solution of HoCl<sub>3</sub>·6H<sub>2</sub>O (10 g) in formic acid (300 ml), bubbling N<sub>2</sub> through the solution.

The melting point of  $\text{HoCl}_3$  is 700 °C; it was measured in a Pt crucible because a melt of holmium chloride reacts slowly with silica, as first described for  $\text{ScCl}_3$  [11]. We could recently show that  $\text{ErCl}_3$  when melted repeatedly in a silica ampoule gives rise to a double peak. The same holds for  $\text{HoCl}_3$ . This is probably the reason for the strongly spreaded melting point values in the literature: 741 °C [12]; 718 °C [7,13]; 704 °C [14].

#### 3.2. Ternary holmium (III) chlorides from solutions

From hydrochloric solutions of ACl and Ho<sub>2</sub>O<sub>3</sub> in the correct molar ratio, ternary chlorides A<sub>3</sub>HoCl<sub>6</sub> with A = Cs, Rb can be obtained by evaporation at ~120 °C. Cs<sub>3</sub>HoCl<sub>6</sub> is formed in the *Pbcm* modification with Z=8 [15]:

$$a = 815.8(3) \text{ pm}; \quad b = 1306.6(5) \text{ pm}; \quad c = 2645.7(7) \text{ pm}$$

With CsCl in a molar ratio 4:1 instead of 3:1, the compound  $Cs_4HoCl_7$  is formed (space group  $R\bar{3}c$  with Z=3 [16]:

$$-a = 772.3(1) \text{ pm}; \quad c = 2599.9(1) \text{ pm}$$

When a solution of CsCl and HoCl<sub>3</sub> in a molar ratio of Cs:Ho=2:1 is evaporated at ~25 °C, the hexahydrate Cs<sub>2</sub>HoCl<sub>5</sub>·6H<sub>2</sub>O is formed: space group  $P2_1/c$  with Z=4

$$a = 834.0(3) \text{ pm};$$
  $b = 944.0(4) \text{ pm};$   
 $c = 2004.0(5) \text{ pm};$   $\beta = 91.28(5)^{\circ} \text{ (still unpublished)}$ 

As found previously [17], anhydrous acetic acid is an excellent solvent system for the preparation of ternary metal chlorides: solutions of HoCl<sub>3</sub> hydrate and alkali metal carbonates in a molar ratio of A:Ho=3:1 were dissolved in acetic acid. When saturating the solutions with HCl gas, the anhydrous compounds A<sub>3</sub>HoCl<sub>6</sub> precipitate. (For A=K it is suitable to use an excess of holmium chloride to avoid the co-precipitation of KCl). The hexachloro holmiates with A=Cs, Rb crystallizes with the Cs<sub>3</sub>BiCl<sub>6</sub> structure (C2/c), K<sub>3</sub>HoCl<sub>6</sub> with the K<sub>3</sub>MoCl<sub>6</sub> structure ( $P2_1/c$ ).

## 3.3. Phase diagrams and crystal structures

Fig. 1 illustrates the results of the DTA investigations. Congruently melting compounds  $A_3HoCl_6$  and  $AHo_2Cl_7$ exist in all systems (A=K, Rb, Cs). All compounds, with the exception of KHo<sub>2</sub>Cl<sub>7</sub>, undergo reversible phase transitions. In the system CsCl/HoCl<sub>3</sub> two additional, incongruently melting compounds exist: Cs<sub>2</sub>HoCl<sub>5</sub> and Cs<sub>3</sub>Ho<sub>2</sub>Cl<sub>9</sub>. The Rb compound Rb<sub>2</sub>HoCl<sub>5</sub> is stable above 414 °C and melts incongruently at 512 °C. By quenching a sample annealed at 450 °C, the main amount, sufficient for an X-ray measurement, could be obtained in a metastable state. In the system KCl/HoCl<sub>3</sub>, the compound K<sub>2</sub>HoCl<sub>5</sub>, decomposing above 415 °C, was found in addition to the compounds K<sub>3</sub>HoCl<sub>6</sub> and KHo<sub>2</sub>Cl<sub>7</sub>, already described by Kurshunov et al. [7].

By analogous indexing of powder patterns the crystal structures of  $K_2HoCl_5$  ( $K_2PrCl_5$  type) and  $Rb_2HoCl_5$  ( $Cs_2DyCl_5$  type) could be determined; the parameters of the unit cell of  $Cs_3Ho_2Cl_9$  [18] were refined. All high-temperature modifications of the compounds  $A_3HoCl_6$ 



Fig. 1. Phase diagrams of the systems  $ACl/HoCl_3$  with A=Cs, Rb, K.

have the cubic elpasolite-type structure. Their lattice parameters were determined at 500 °C. L-Cs<sub>3</sub>HoCl<sub>6</sub> crystallizes in the space group C2/c (Cs<sub>3</sub>BiCl<sub>6</sub>-type), L-K<sub>3</sub>HoCl<sub>6</sub> in  $P2_1/c$  (K<sub>3</sub>MoCl<sub>6</sub> type). All unit cell parameters together with the values of Meyer for the other compounds are compiled in Table 1.

As found by DSC,  $K_3$ HoCl<sub>6</sub> has another phase transition at 137 °C, which is not shown in Fig. 1. At this temperature, the monoclinic *a*- and *c*-axis have the same value:

 $a = c = 1308.0 \text{ pm}; \quad b = 745 \text{ pm}; \quad \beta = 109.4^{\circ}.$ 

For this condition an orthorhombic cell can be given based on the diagonal of the monoclinic *ac*-plane.

Further investigations of the consequences of this feature are conducted with the analogous modification of  $K_3$ ErCl<sub>6</sub>.

Table 1						
Unit cell	parameters	of	ternary	holmium	(III)	chlorides

# 3.4. Solution calorimetry and e.m.f. measurements

The solution enthalpy of HoCl<sub>3</sub> was found to be  $-209.4\pm1$  kJ mol<sup>-1</sup> (literature: -210.25 [22]; -209.20 [23]; -213.43 [24]). The solution enthalpies for the alkali metal chlorides were taken from previous investigations; i.e., CsCl=18.1(2); RbCl=17.6(2); KCl = 17.9(1) kJ mol<sup>-1</sup>. The results of the measurements are given in Table 2. Because the not-congruently melting compounds A<sub>2</sub>HoCl<sub>5</sub> could not be obtained by annealing or quenching (Rb<sub>2</sub>HoCl<sub>5</sub>). For this reason, no solution enthalpies were measured. E.m.f. measurements could be obtained for all compounds, except the HoCl<sub>3</sub> richest, AHo<sub>2</sub>Cl<sub>7</sub>. For these compounds, the potential differences were higher than ~500 mV; according to former experiences, the e.m.f. cells break down at voltages of this magnitude.

Compound	Space	a/pm	b/pm	c/pm	β°	$V_{\rm m}/{\rm cm}^3~{\rm mol}^{-1}$	
	group						
H-Cs <sub>3</sub> HoCl <sub>6</sub>	Fm3m	1152.2(2)				230.3	
H-Rb <sub>3</sub> HoCl <sup>a</sup> <sub>6</sub>	Fm3m	1121.4(2)				212.3	
H-K,HoCl	Fm3m	1095.2(1)				197.8	
L-Cs <sub>3</sub> HoCl <sub>6</sub>	C2/c	2692.7(8)	813.1(2)	1313.9(5)	100.23(3)	213.1	
L-Rb <sub>3</sub> HoCl <sub>6</sub> [19]	C2/c	2577.2(3)	786.8(1)	1280.2(2)	99.56(1)	192.7	
L-K <sub>3</sub> HoCl <sub>6</sub>	P2,/c	1308.4(7)	772.1(4)	1263.6(8)	110.02(4)	180.6	
Cs <sub>2</sub> HoCl <sub>5</sub> [20]	Pnma	951.5(2)	745.4(1)	1520.2(2)		162.4	
Rb <sub>2</sub> HoCl <sub>5</sub>	Pnma	957.0(4)	727.9(2)	1464.2(3)		153.6	
K <sub>2</sub> HoCl <sub>5</sub>	Pnma	1264.2(4)	856.2(4)	792.8(2)		129.2	
Cs <sub>3</sub> Ho <sub>2</sub> Cl <sub>9</sub>	RĴc	1311.3(3)		1842.9(5)		275.4	
CsHo <sub>2</sub> Cl <sub>7</sub> [21]	Pnma	695.6(1)	1264.7(4)	1334.3(2)		176.7	
RbHo <sub>2</sub> Cl <sub>7</sub> [21]	Pnma	692.1(1)	1263.6(3)	1286.9(1)		169.5	
KH0 <sub>2</sub> Cl <sub>7</sub> [21]	P2,/c	686.7(7)	1258.3(2)	1272.1(2)	89.36(3)	165.5	

<sup>a</sup> Measured at 500 °C.

Table 2 Solution enthalpies  $\Delta_{sol}H^{\circ}$  and enthalpies of formation from the binary compounds,  $\Delta_{i}H^{\circ}$  (in KJ mol<sup>-1</sup>)

Compound	$\Delta_{soi}H_{298}^{\circ}$	$\Delta_{ m f} H_{ m 293}^{\circ}$
Cs <sub>3</sub> HoCl <sub>6</sub> (Pbcm)	-60.1(3)	- 95.0
$Cs_{HoCl_{6}}(C2/c)$	- 60.5(5)	-94.6
1/2 Cs, Ho, Cl,	- 117.9(6)	-64.4
1/2 CsHo,Cl,	-167.6(1)	- 32.8
Rb, HoCl	-79.8(3)	- 76.8
1/2 RbHo,Cl,	-168.1(1)	- 32.5
K,HoCl	-102.2(8)	- 53.5
1/2 KH0 <sub>2</sub> Cl <sub>7</sub>	-173.2(4)	-27.3

The measured regression and Gibbs-Helmholtz equations,  $\Delta_r G^\circ = \Delta_r H^\circ - \Delta_r S^\circ T$ , for the reaction in the cell are listed below. They are mean values of two measurements. The range of error was smaller than 1 kJ mol<sup>-1</sup> for the energy values and 0.8 JK<sup>-1</sup>mol<sup>-1</sup> for the entropies.

Reaction: 
$$CsCl + Cs_{0.5}HoCl_{3.5} = Cs_{1.5}HoCl_{4.5}$$
  
 $(T = 580-670 \text{ K})$   
e.m.f./mV = 335.2 + 0.0208 T/K  
 $\Delta_r G^{\circ}/kJ \text{ mol}^{-1} = -32.3 - 0.0020 T/K$   
Reaction: 0.5  $CsCl + Cs_{1.5}HoCl_{3.5} = Cs_2HoCl_5$   
 $(T = 600-660 \text{ K})$   
e.m.f./mV = 364.0 - 0.0698 T/K  
 $\Delta_r G^{\circ}/kJ \text{ mol}^{-1} = -17.6 + 0.0034 T/K$   
Reaction:  $CsCl + Cs_2HoCl_5 = Cs_3HoCl_6$   
 $(T = 570-660 \text{ K})$   
e.m.f./mV = 174.4 + 0.0964 T/K  
 $\Delta_r G^{\circ}/kJ \text{ mol}^{-1} = -16.8 - 0.0093 T/K$ 

Rubidium compounds:

Reaction: 2.5 RbCl+Rb<sub>0.5</sub>HoCl<sub>3.5</sub> = Rb<sub>3</sub>HoCl<sub>6</sub>  
(
$$T$$
=600-690 K)  
e.m.f./mV = 163.3 + 0.1536 T/K  
 $\Delta_r G^{\circ}$ /kJ mol<sup>-1</sup> = -39.4 - 0.0371 T/K

## Potassium compounds:

Reaction:  $1.5\text{KCl} + \text{K}_{0.5}\text{HoCl}_{3.5} = \text{K}_{2}\text{HoCl}_{5}$  (T = 600-640 K)e.m.f./mV = 265.5 - 0.0759 T/K  $\Delta_{r}G^{\circ}/\text{kJ} \text{ mol}^{-1} = -38.4 + 0.0110 \text{ T/K}$ Reaction:  $\text{KCl} + \text{K}_{2}\text{HoCl}_{5} = \text{K}_{3}\text{HoCl}_{6}$  (T = 600-640 K)e.m.f./mV = -118.0 + 0.4807 T/K $\Delta_{r}G^{\circ}/\text{kJ} \text{ mol}^{-1} = 11.4 - 0.0464 \text{ T/K}$ 

In Table 3, the enthalpies from e.m.f. measurements and solution calorimetry are compared and mutually completed:  $\Delta_t H^\circ$  for the compounds AHo<sub>2</sub>Cl<sub>7</sub> are taken from

solution calorimetry, for the compounds  $A_2HoCl_5$  from  $\Delta_r H^\circ$  ( $A_{0.5}HoCl_{3.5}$ ) and  $\Delta_r H^\circ$ ( $A_2HoCl_5$ ).

The differences between both sets are small for the  $HoCl_3$  rich compounds, larger for the 3:1 compounds with Cs and Rb.

A ternary compound is stable when the free enthalpy of formation from the two adjacent compounds in its pseudobinary system, the free enthalpy of syn-reaction,  $\Delta_{syn}G^{\circ}$ , is negative. At low temperature the entropy term  $\Delta S \cdot T$  is neglegible; then it is sufficient that  $\Delta_{syn}H^{\circ}$  is negative (exothermic syn-reaction). We have calculated such synreaction energies: for the AHo<sub>2</sub>Cl<sub>7</sub> compounds,  $\Delta_{syn}H^{\circ}$ values can be taken directly from Table 3, for all other compounds Gibbs-Helmholtz equations from e.m.f. measurements, setting  $\Delta_{f}G^{\circ}$  (A<sub>0.5</sub>HoCl<sub>3.5</sub>)=0 were used. For the compounds A<sub>3</sub>HoCl<sub>6</sub> the neighbour is ACl, therefore it is  $\Delta_{r}G^{\circ} = \Delta_{syn}G^{\circ}$ . For Rb<sub>2</sub>HoCl<sub>5</sub> no thermodynamic values could be measured.

Syn-reaction enthalpies for compounds A<sub>0.5</sub>HoCl<sub>3.5</sub>:

 $\frac{1/3 \text{ Cs}_{1.5}\text{HoCl}_{4.5} + 2/3 \text{ HoCl}_{3} = \text{Cs}_{0.5}\text{HoCl}_{3.5}}{\Delta_{\text{syn}}H^{\circ} = -11.3 \text{ KJ mol}^{-1}}$   $\frac{1/6 \text{ Rb}_{3}\text{HoCl}_{6} + 5/6 \text{ HoCl}_{3} = \text{Rb}_{0.5}\text{HoCl}_{3.5}}{\Delta_{\text{syn}}H^{\circ} = -19.7 \text{ KJ mol}^{-1}}$   $\frac{1/4 \text{ K}_{2}\text{HoCl}_{5} + 3/4 \text{ HoCl}_{3} = \text{K}_{0.5}\text{HoCl}_{3.5}}{\Delta_{\text{syn}}H^{\circ} = -10.9 \text{ KJ mol}^{-1}}$ 

Gibbs-Helmholtz equations for  $\Delta_{syn}G^{\circ}$ :

2/3  $Cs_2HoCl_5 + 1/3 Cs_{0.5}HoCl_{3.5} = Cs_{1.5}HoCl_{4.5}$   $\Delta_{syn}G^{\circ}/KJ mol^{-1} = 1.0 - 0.0029 T/K$   $(\Delta_{syn}G^{\circ} = 0 \text{ at } 345 \text{ K} (72 °\text{C}))$ 1/3  $Cs_3HoCl_6 + 2/3 Cs_{1.5}HoCl_{4.5} = Cs_2HoCl_5$   $\Delta_{syn}G^{\circ}/KJ mol^{-1} = -6.1 + 0.0053 T/K$   $CsCl + Cs_2HoCl_6 = Cs_3HoCl_6$   $\Delta_{syn}G^{\circ}/KJ mol^{-1} = -16.8 - 0.0093 T/K$ 2.5  $RbCl + Rb_{0.5}HoCl_{3.5} = Rb_3HoCl_6$   $\Delta_{syn}G^{\circ}/KJ mol^{-1} = -39.4 - 0.0371 T/K$ 0.6  $K_3HoCl_6 + 0.4 K_{0.5}HoCl_{3.5} = K_2HoCl_5$   $\Delta_{syn}G^{\circ}/KJ mol^{-1} = -22.2 + 0.0322 T/K$   $(\Delta_{syn}G^{\circ} = 0 \text{ at } 689 \text{ K} (416 °C)$ From DTA heating curves: 415 °C.)  $KCl + K_2HoCl_5 = K_3HoCl_6$  = 11.4 - 0.0464 T/K $(\Delta_{syn}G^{\circ} = 0 \text{ at } 246 \text{ K})$ 

## 4. Discussion

- There is an analogy between the systems  $ACl/HoCl_3$ and  $ACl/DyCl_3$  (A = K, Rb, Cs):
- Congruently melting compounds ALn<sub>2</sub>Cl<sub>7</sub>, (Ln=Dy, Ho) are formed exothermally from their neighbouring compounds and from ACl and LnCl<sub>3</sub>.

# Table 3

Reaction and formation enthalpies of ternary holmium chlorides (in kJ mol<sup>-1</sup>)

$CsCl + Cs_3$	HoCl <sub>6</sub> Cs <sub>2</sub> ] I	HoCL I	1/2 Cs <sub>3</sub>	Ho <sub>2</sub> Cl,	1/2 Cs	Ho <sub>2</sub> Cl <sub>7</sub>	HoCl <sub>3</sub>	
	158	E	17.6	-32.3	┸╌┼╸	32.8		
	< [10,0]	t –				-65.1		
EMF				4				
(Δ <mark>,</mark> H°)		•		-82.7	′ <u> </u>			
	<b></b>	·	-99.5					
			94.6					
CsCI+HoCl <sub>3</sub>			27.0		[-			
Solution.				82.0	<u></u>			
calorimetry		[		-		-64.4		
(∆ <sub>r</sub> H°)						660		
-					-	-32.8		
RbCl+ Rb <sub>3</sub>		(Rb <sub>2</sub> H	oCl <sub>5</sub> )	1/2 RbH	lo <sub>2</sub> Cl <sub>7</sub>	22.5	HoCl <sub>3</sub>	
	-3	9.4				-32.5		
EMF			-71 (	.				
(Δ <sub>r</sub> H°)								
		[						
KUCI + HUCI3								
Solution-						-32.5		
calorimetry		Ì						
(∆ <sub>r</sub> H°)		1		_				
			-76	5.8				
	1	1		I			1	
KCI+ K.F	loCl.	K Ha	ri -	1/2 71	6.01		HoCl.	
1101 1 132	]	K2110				-27.3		
	+11.4	L	-32	<u>.4</u>				
EMF			-27	7.0				
(A <sub>1</sub> H*)			-					
				+	[	·		
KC1+ H-C1			_					
NU T 110U3				53.5		· · · · · · · · · · · · · · · · · · ·		
Solution-			_^	26.2	[			
calorimetry								
(∆ <sub>f</sub> H⁰)		ŀ	4			-65.7		
-								
							l	

- The compounds Cs<sub>2</sub>LnCl<sub>5</sub> crystallize in the Cs<sub>2</sub>DyCl<sub>5</sub> structure with octahedral surroundings of the Ln<sup>3+</sup> ions, while the potassium compounds K<sub>2</sub>LnCl<sub>5</sub> have CN 7 (K<sub>2</sub>PrCl<sub>5</sub> type). Both compounds are formed exothermally.
- The compounds Cs<sub>3</sub>LnCl<sub>6</sub> and Rb<sub>3</sub>LnCl<sub>6</sub> have exothermal syn-reaction enthalpies too. The high-temperature modifications (transition temperature ~400 °C) have extremely high melting points near 900 °C. The latter is also true for the potassium compounds. However, they have endothermic syn-reaction enthalpies and exist only at elevated temperatures K<sub>3</sub>DyCl<sub>6</sub> above 312 K, K<sub>3</sub>HoCl<sub>6</sub> above 246 K by a sufficiently high gain in syn-reaction entropy (46.5 and 46.4 JK<sup>-1</sup>mol<sup>-1</sup>)

However, there are also differences between both systems.

- 1. For K<sub>3</sub>HoCl<sub>6</sub>, except for L-K<sub>3</sub>HoCl<sub>6</sub> (K<sub>3</sub>MoCl<sub>6</sub>-type) and H-K<sub>3</sub>HoCl<sub>6</sub> (elpasolite-type), an additional modification exists between 137 °C and 378 °C with a presumably orthorhombic unit cell.
- 2. Holmium is the first element in the series starting with lanthanum, for which a 3:2 compound  $Cs_3Ho_2Cl_9$  exists. In this enneachloride, isolated pairs of face-sharing octahedra exist. Such double octahedra  $[Ho_2Cl_9]^{3-}$  are less deformable than isolated octahedra. Therefore, they are only formed if the radius ratio  $r_{Ln}^{3+}/r_{Cl}^{-1}$  is near to the ideal value for six ligands, i.e. 0.41. With  $r_{Ho}^{3+} = 0.894$  Å [25] and  $r_{Cl}^{-} = 1.81$  Å, the ratio is 0.49. An analogous Rb compound does not exist because the Rb<sup>+</sup> ion is too small to be surrounded by the necessary twelve Cl<sup>-</sup> ions.
- 3. In the Rb systems the compound  $Rb_2HoCl_5$  exists having the  $Cs_2DyCl_5$  structure with corner connected [HoCl\_4Cl\_{2/2}] octahedra. The analogous compounds with Dy and Tb do not exist, while  $Rb_2GdCl_5$  crystallizes in the  $K_2PrCl_5$  type with CN=7 for  $Ln^{3+}$ .  $Rb_2HoCl_5$  is stable at temperatures higher than 414 °C.

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